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Br···Br and Br···H Interactions in Action: Polymorphism, Hopping, and Twinning in 1,2,4,5-Tetrabromobenzene

H. F. Lieberman, R. J. Davey,* and D. M. T. Newsham

Colloids, Crystals and Interfaces Group, Department of Chemical Engineering, UMIST,
Manchester M60 1QD, U.K.

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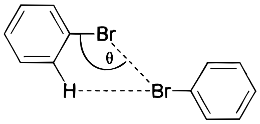
The nature and importance of nonbonded halogen−halogen and halogen−hydrogen interactions in molecular crystals continues to attract significant attention. Here, we report the manifestation of such interactions in the twinning and polymorphism of 1,2,4,5-tetrabromobenzene. A combination of molecular modeling and experimental studies using DSC, hot stage optical microscopy, and in situ powder X-ray diffraction is used to explore the mechanism of phase transition and understand the basis of twin formation in this material. The propensity to twin, the observed polymorphism, and the fact that crystals hop as they transform are all consequences of Br···Br and Br···H interactions.

Introduction

The importance and nature of halogen−halogen and halogen−hydrogen interactions as driving forces for crystal engineering and molecular recognition has received significant attention in recent years.[1] Desiraju and Parthasrathy [2] surveyed existing crystal structures in an attempt to explore the nature of halogen−halogen interactions, whereas Price et al.[3] showed that for chlorine−chlorine interactions the nonspherical atomic charge distribution has to be included in any attempt to model the interaction. In the case of bromine bonded to a phenyl ring, Murray et al.[4] have given further evidence of this nonsphericity and demonstrated that its electrostatic potential is largely negative with a small positive cap. This means that, in agreement with the analysis of Lommerse et al.,[5] with this configuration bromine can interact with a nucleophile “head-on” and an electrophile “side-on” and hence stabilize the motif (**1**), which includes both bromine−bromine and bromine−hydrogen interactions, as shown schematically in Figure 1. The importance of this motif and its stability have been reviewed recently by Navon et al.[6] who find a stabilization of some 0.45 kJ mol^{-1} for an isolated motif (**1**) relative to infinite separation. To explore the physical manifestations of these interactions, we have chosen the specific case of 1,2,4,5-tetrabromobenzene (TBB). This molecule crystallizes not only as twins but also in two polymorphic forms: the β phase, which is stable at room temperature,[7] and the γ phase, which is stable above 46 °C.[8] In both structures, bromine−bromine and bromine−hydrogen interactions play a significant role in controlling the molecular packing, and we have chosen to investigate further the crystal chemistry of this material as an example of how such interactions can control crystallization and phase behavior.



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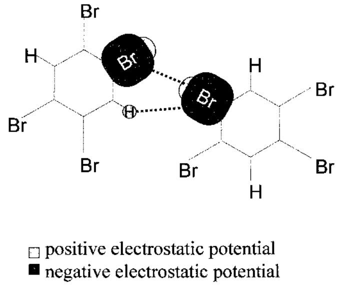

Figure 1. Schematic representation of the electrostatic potential around bromine atoms.

Crystallography of 1,2,4,5-Tetrabromobenzene. Both β and γ structures have the space group $P2_1/a$[7,8] and each contains half a molecule in the asymmetric unit, so that there are only two independent bromine atoms. For the β structure, $a = 10.323$, $b = 10.705$, and $c = 4.018$ Å, with $\beta = 102.37°$, whereas for the γ structure, $a = 10.00$, $b = 11.18$, and $c = 4.07$ Å, with $\beta = 103.80°$. The densities are 3.015 and 2.955g cm^{-3} for β and γ, respectively. Each polymorph is constructed from sheets of tetrabromobenzene molecules that lie approximately in the $(20\bar{1})$ plane; they deviate from coplanarity by 14.1° in the case of the β polymorph and

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Table 1. C-H···Br and Br···Br Contacts

	Br···Br (Å)	Br···H (Å)	θ (°)
from Navon et al.[6,a]	3.40−3.70	2.90−3.90	82.41−123.1
β (Br(1))	3.619	2.994	100.3
β (Br(2))	3.923	3.409	105.4
γ (Br(1))	3.729	3.232	102.7
γ (Br(2))	3.710	3.185	102.6

[a] A total of 10 structures are summarized in this table.

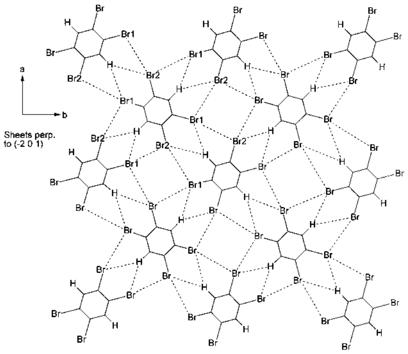

Figure 2. Sheet $(20\bar{1})$ in the γ structure of TBB showing (- - -) the nonbonded bromine−hydrogen and bromine−bromine interactions.

7.9° in the γ structure and adopt a herringbone packing along the [102] direction. The intersheet distance is 3.186 and 3.464 Å in the β and γ structures, respectively. Table 1 lists for each structure the distances of the Br···Br and C−H···Br contacts within the $(20\bar{1})$ planes, the C−Br···Br angle, θ, and the range of values quoted by Navon et al.[6]

Figure 2 shows a projection of the molecular arrangement in the $(20\bar{1})$ sheets for the γ structure, highlighting the motif (**1**) together with the Br···Br interactions. The equivalent projection for the β structure differs only in the absence of one of the Br···Br contacts and the somewhat less symmetrical nature of the motif (**1**).

In addition to polymorphism, Gafner and Herbstein[7,8] reported that crystals of both structures of TBB form twinned crystals in which the components are related by the (110) mirror plane. Recent lattice energy calculations, carried out by Krafczyk et al.[9] for the β structure predict the two halves of this twin to be displaced relative to one another by $[\bar{1}10]/2$ and $c/2$ and to have a lattice energy 2.8% lower than that of a single crystal.

Experimental Section

Crystal Growth. Crystals of β-TBB were grown at 25 °C from supersaturated solutions in toluene, *p*-xylene, acetone, 1,2-dichlorobenzene, and mixtures of these by cooling saturated solutions with and without stirring.

Hot Stage Microscopy. Single crystals of dimensions up to 1200×200 μm were observed, during heating (2 °C/min), in transmitted light using a Zeiss Axioplan2 polarizing microscope fitted with a Linkam hot stage. To assess the impact of twinning on the phase transition, 10 twinned and 10 untwinned crystals were examined. Occasionally, some β crystals would not transform by heating alone; in these cases, it was found that transformation could be induced by application of slight stress by touching the crystal with a needle. Such crystals were not included in the results reported here.

Thermochemistry. The enthalpy and temperature of the $\beta \Rightarrow \gamma$ phase transition of TBB was measured using a Mettler 4000 differential scanning calorimeter with a heating rate of 10 °C/min.

X-ray Diffraction. To obtain structural data on the phase transition, powder X-ray diffraction was performed on a Scintag diffractometer in 5 °C steps at temperatures from 25 to 55 °C. Samples were used unground in order to prevent any pressure-induced transformation. The twin plane in selected β single crystals was determined by Weissenberg X-ray photography to compare with previous reports.[7,8]

Molecular Modeling. Calculations have been carried out using *Gaussian94*[10] on an isolated TBB molecule and on the motif (**1**) as it occurs in the β polymorph. Single-point Hartree−Fock calculations were performed at the STO-5G* level with heavy atom coordinates taken from the crystal structures[7,8] and hydrogens fitted using the PM3 method of MOPAC with bond lengths adjusted to 1.083 Å. The electrostatic potential from the calculated wave function was visualized using MOLDEN.[11] A twin interface in the β structure was visualized using CERIUS molecular modeling software.[12] Two portions of crystal were created related by reflection through the twin plane $(\bar{1}10)$: one portion was moved by $^1/_2$ lattice repeats along c and $[\bar{1}10]$ directions,[9] and the two parts were docked by hand while close contacts were monitored.

Results and Discussion

Single-Crystal Experiments. The best quality β crystals were obtained from toluene or *p*-xylene solution and appeared as mixtures of both single and twinned crystals elongated about their [001] axes. Twins were easily identified by the line running along the crystal length parallel to the c axis. Stirring of the crystallizing solutions with a magnetic stirrer produced more single crystals, and increasing the supersaturation produced more twins. A few crystals produced from 1,2-dichlorobenzene without stirring grew as lamellar twins although normally it was evident that twinning occurred at nucleation creating hemihedral twins in which each member of the pair was of essentially the same size. Overall, although it was possible to hand select individual twinned and untwinned crystals for examination by optical microscopy, it proved impossible to produce larger samples of pure twinned or untwinned for DSC and powder XRD. Consequently, these techniques utilized samples containing both twinned and untwinned crystals.

Hot stage microscopy revealed that the phase transition between β and γ is accompanied by the crystals hopping to heights of several times their own length (i.e. ≈centimeters), a feature that made experimental observation somewhat problematic. It was found that such hopping, which took place on the time scale of 1/25 s and led to breakage of crystals into smaller twinned fragments, prevented any attempt to observe in detail a crystal as it changed phase. Even when constrained with a small amount of grease, no change in the

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morphological appearance of crystals could be discerned. The transition temperature as measured by the temperature at which hopping occurred was found to vary slightly from crystal to crystal. Measurements on 10 single and 10 twinned crystals gave the mean of the former as 45.0 °C (standard deviation 0.35) and of the latter as 45.5 °C (standard deviation 0.60). A student's *t* test indicated that the difference in these means is significant at the 98% confidence limit. Thus, twinned crystals tended to transform at about 0.5 °C higher than single crystals. This stabilization of the β structure against phase transition due to twinning mirrors the behavior observed in terephthalic acid[13] where multiple twinning stabilized a metastable polymorph indefinitely at room temperature.

Thermochemistry. The DSC data gave the enthalpy of the phase transition to be 0.315 kJ mol^{-1} and a peak β to γ transition temperature of 45.5 °C, which is consistent with the single-crystal observations. The enthalpy of melting and the melting point taken from the same data are 26.024 kJ mol^{-1} and 180.4 °C, respectively. These data agree well with previously published thermochemical data,[14,15] which reported a transition temperature and enthalpy of 46 °C and 0.355 kJ mol^{-1} and an enthalpy and temperature of melting of 27.88 kJ mol^{-1} and 180 °C.

Crystal Hopping and Phase Transformation. The phenomenon of crystal hopping during a solid-state phase transition has been cited in the literature on several occasions for organic molecular crystals: (±)-3,4-di-*O*-acetyl-1,2,5,6-tetra-*O*-benzyl-*myo*-inositol,[16] *ttatt*-perhydropyrene,[17] oxitropium bromide,[18] terephthalic acid,[13] and 4,5-bis(fluorodinitromethyl)-2-methoxy-1,3-dioxolane[19] all exhibit this phenomenon.

Of these, all but the last have been fully characterized by thermal analysis and all transitions are, as in the current case of TBB, endothermic. Such thermal behavior indicates that the transitions are entropy-driven (order−disorder), and although this is not unusual for hydrogen-bonded systems due to proton disordering,[13] it is not clear whether it is implicated in the hopping process. Previous explanations of the hopping effect have suggested that molecular movements within a layered structure[17,18] are responsible. In the case of tetrabromobenzene, discussed here, it is evident from the crystallography that the molecules themselves move very little within the $(20\bar{1})$ layers. On heating, a slight twisting motion must occur such that the angle between neighboring rings decreases from 22.6° in the β structure to 13.7° in the γ structure with the molecules becoming *more* coplanar and the Br(2)···H distance becoming shorter. This is confirmed by previous spectroscopic data[20] and results in a more symmetrical motif (**1**) in the γ form compared to that of the β form. In thermodynamic terms, at constant pressure, the changes in enthalpy and energy due to transformation are related by

$$\Delta H = \Delta E + p\Delta V$$

in which $p\Delta V$ (ΔV is the volume change of a crystal on transformation) is the work done against the environment during the transition. If this work is responsible for the hopping then it follows that

$$p\Delta V \geq mgh$$

and hence that

$$h \approx (p/g)[1/\rho_\gamma - 1/\rho_\beta]$$

in which g is the acceleration due to gravity, p is atmospheric pressure, ρ is the respective crystal density of each form, h is the hopping height, and m is the mass of a crystal. By using the density data given above, the value of h can be calculated to be 65 mm and is independent of the mass of the crystal. Although the value of h has not been specifically measured in this work, it is estimated to be on the order of a few centimeters, which is not only of the same magnitude as previous reports[16,17,18] but also consistent with the thesis proposed here that the phenomenon of crystal hopping is a manifestation of the work done by the crystal against its surroundings during the transition. This work results from the change in crystal density, which in turn reflects the modification of molecular packing due, at least in part, to the change in the geometry of the Br···Br and Br···H interactions.

X-ray Powder Diffraction. The two extreme powder patterns, those for 25 and 55 °C, are shown in Figure 3. The major peak in all patterns is the (220) peak at $2\theta = 24.05°(\beta)$ and $24.20°(\gamma)$. This is due to preferred orientation along the (001) needle axis of the crystal. As shown in Figure 4a,b, the main shifts in peak positions occurring on phase transformation are those corresponding to (hk0) planes. An examination of the unit cell parameters indicates why this should be the case because a and b change by 3 and 4%, respectively, (0.323 and 0.475 Å) when the unit cell expands from the β to the γ structure, whereas the c cell parameter increases only by 1% (0.052 Å). In addition, Figure 4c shows how the intensity of $(20\bar{1})$ is enhanced upon transformation to the γ polymorph: below the transition temperature, it is less than 10%, whereas above, it is between 30 and 40%. This confirms the importance of the $(20\bar{1})$ molecular sheets that contain the aromatic rings, which are more in plane with $(20\bar{1})$ in the γ than in the β polymorph, thus increasing the intensity of the related reflection.

Modeling of Molecular Interactions and the Twin Interface. The overall importance of Br···Br and Br···H interactions in these crystals were further explored by extending the calculations of Navon et al.[6] to a consideration of the electrostatic potential map, Figure 5, through two molecules taken from the $(20\bar{1})$ plane of the β polymorph. From this plot, the interaction between

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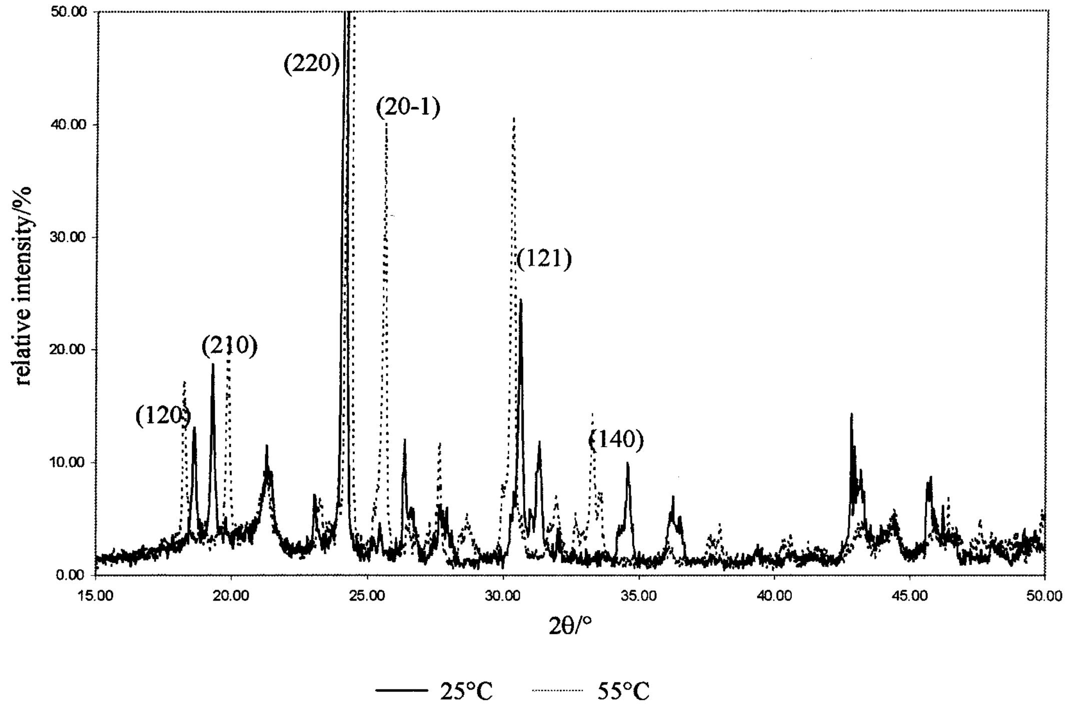

Figure 3. Powder XRD patterns of TBB at 25 and 55 °C. Major reflections as indicated.

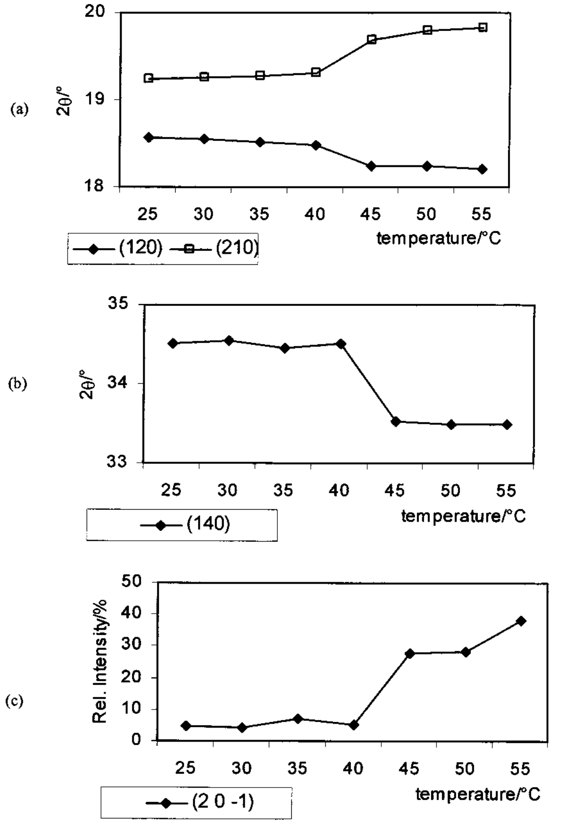

Figure 4. Temperature dependence of the powder XRD patterns of TTB: (a) and (b) change in diffraction angle with temperature of the (120), (210), and (140) reflections, and (c) change in intensity of the $(20\bar{1})$ reflection.

Figure 5. Calculated electrostatic potential for two molecules taken from the $(20\bar{1})$ sheet of the β structure (solid and dashed lines are positive and negative contours, respectively, drawn at intervals of 0.05 a.u. up to a maximum of 0.5 a.u. for the sake of clarity. The thick solid line is the zero contour).

H1 and both Br atoms of a neighboring molecule (shown by the dotted straight lines) can be seen, even though the distance H1···Br(2) (3.409 Å) is significantly longer than H1···Br(1) (2.994 Å). The halogen interaction Br(1)···Br(2) can also be seen; arising from the small positive cap on Br(1) that interacts with the negative region around Br(2). This is consistent with the earlier work of Murray et al.[4] and Price et al.[3] No such interaction is possible between the related Br(1) and Br(2) atoms due to unfavorable geometric constraints. Overall, it is these hydrogen−bromine and bromine−bromine interactions that allow the TBB molecules to adopt layer structures, leading ultimately to the observed polymorphs with their hopping and order−disorder transition.

By considering the twinning of the β form, the model shown in Figure 6 has been created in order to visualize

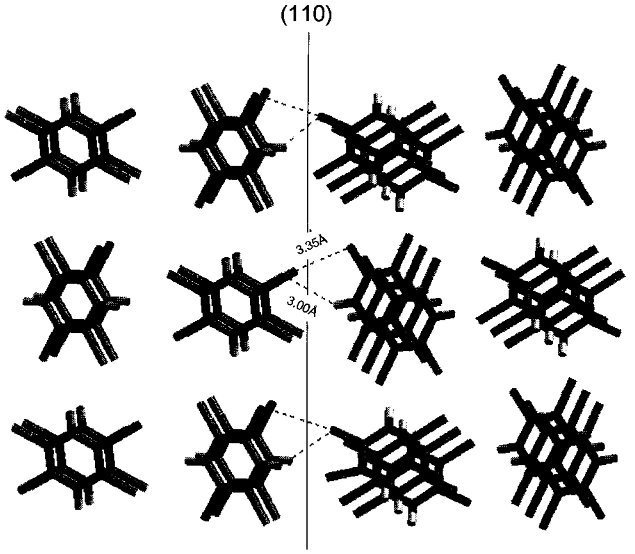

Figure 6. Visualization of the twin interface showing close bromine−bromine and bromine−hydrogen contacts.

the twin interface. In constructing this model, Br···Br and Br···H distances of 3.35 and 3.00 Å, respectively, were found to be easily accessible without incurring other significantly unfavorable close contacts. Given the approximate nature of this construction and by comparing these distances with those in Table 1, it seems reasonable to conclude that the intermolecular interactions responsible for stabilizing both the β and γ sheets are also implicated in stabilizing the twin interface in β crystals. The molecules that form the twinned interface across the (110) mirror plane are, of course, not coplanar as they are in the sheets: the angle between molecules across the twin plane is 49°. Because this angle is typical of many aromatic "herringbone structures" where it is a means of maximizing C···C and C···H interactions,[1] the possibility that such interactions were also responsible for stabilizing twin interface was checked. It was clear that the steric clashes involved ruled out this possibility, and it is concluded that it is the electrostatic potential on the bromine atom shown in Figure 1 that allows the establishment of favorable Br···Br and Br···H interactions across the twin plane. The modest stabilization of twinned crystals against phase transformation presumably results from the twin plane effectively pinning the molecular sheets and preventing their expansion from the β to the γ structure.

Conclusions

The crystal chemistry of 1,2,4,5-tetrabromobenzene, as reflected in the formation of twinned crystals and enantiotropically related polymorphic forms, appears to be dominated by intermolecular Br···Br and Br···H interactions. These result from the nonuniformity of the electrostatic potential on the bromine atom and give rise to an order−disorder phase transition together with crystals that twin and hop when undergoing phase transformation between β and γ structures.

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